

PATENT SPECIFICATION

(11) 1330 932

1330 932

NO DRAWINGS

- (21) Application No. 43248/71 (22) Filed 16 Sept. 1971
 (31) Convention Application No. 80509 (32) Filed 16 Sept. 1970 in
 (33) Japan (JA)
 (44) Complete Specification published 19 Sept. 1973
 (51) International Classification C08G 5/06 37/14
 (52) Index at acceptance



C3R 1C12 1C14B 1C25 1C28A 1C29 1C33X 1C8R 1C9Q
 1D2A 1D2BX 1D2C 1D2E 1E2B 1E7A 1L1B 1L2X
 1L6D 1L6G 1N1H 1N2H 1N2N 1N2Q1 1N2QX
 1N2S 1N4
 G2C C4C5B C4D3D C4G2

(54) PHENOLIC RESIN CONDENSATION PRODUCT AND LIGHT-SENSITIVE COMPOSITIONS CONTAINING IT

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese body corporate of 1—10, 3-chome, Nihonbashi-Muro-machi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a light-sensitive composition useful for positive-positive type photomechanical process, which contains a condensation product of o-benzoquinonediazide or o-naphthoquinonediazide sulfonyl chloride with a bisphenol-formaldehyde resin. More particularly, the invention pertains to a light-sensitive composition applied to the so-called presensitized plate (hereinafter referred to as "PS plate") which is of the type used by coating the composition on a support followed by drying.

It is well known that esters or amides of o-quinonediazide sulfonic acid are used as light-sensitive compositions for photomechanical processes. These o-quinonediazide compounds have such property that they are decomposed by application of active rays to form free carboxylic acids. By utilization of this property, there is adopted such procedure that only exposed portions are dissolved and removed by use of an aqueous alkaline solution, e.g. an aqueous sodium metasilicate solution, to form images comprised of unexposed portions. Compounds of this kind have been known in large numbers hitherto, and most of them are low molecular weight compounds. If these o-quinonediazide compounds are used singly as light-sensitive materials, not only crystals come to deposit but also the resulting images are low in mechanical strength, so that it is difficult to obtain therefrom a large number of copies by printing. Accordingly, an alkali-soluble resin such as, for example, phenol-formaldehyde novolak resin, shellac or styrene-maleic anhydride resin is used as a carrier together with the o-quinonediazide compound. When this system is subjected to imagewise exposure to light and then treated with an aqueous alkaline solution, the alkali-soluble resin in unexposed portions is inhibited from dissolution due to the alkali resistance of said portions, thereby forming an image. Particularly in the case where the resulting image is desired to be engraved on a metal support, and in the case where the resulting image is desired to be used directly as a printing plate, it is important to use an alkali-soluble resin having excellent properties.

That is, when the o-quinonediazide compound is used together with an alkali-soluble resin as a carrier, the light-sensitive layer is prevented from deposition of crystals and the resulting image is inhibited from deterioration in mechanical strength.

In view of the above, United States Patent Specification No. 3,046,120 has proposed the use of a high molecular weight compound prepared by condensing an alkali-soluble phenol formaldehyde novolak resin or o-cresol-formaldehyde novolak resin with a sulfonyl chloride of o-benzoquinonediazide or o-naphthoquinonediazide. However, when the compound disclosed in said United States patent is used, the resulting image portion suffers from dissolution by attack of an aqueous alkaline solution and is low in adhesion to a support, so that the image is inferior in mechanical strength. Moreover, the image portion has only a poor oleophilic property.

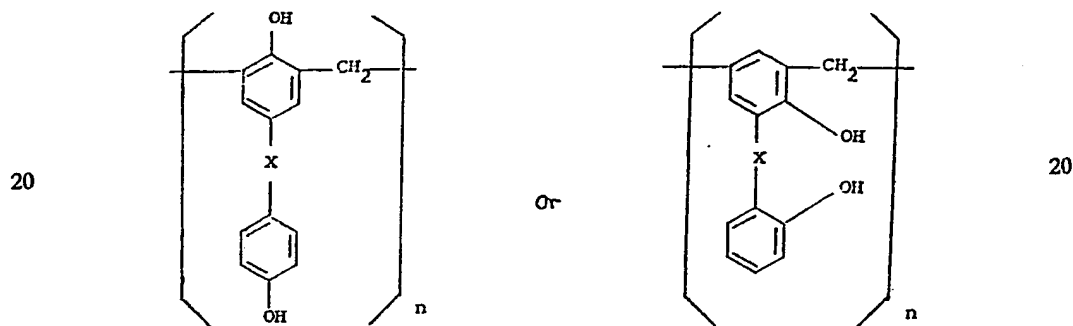
An object of the present invention is to provide a photoengraving light-sensi-

tive composition which mitigates or overcomes the drawbacks of conventional light-sensitive compositions of this kind.

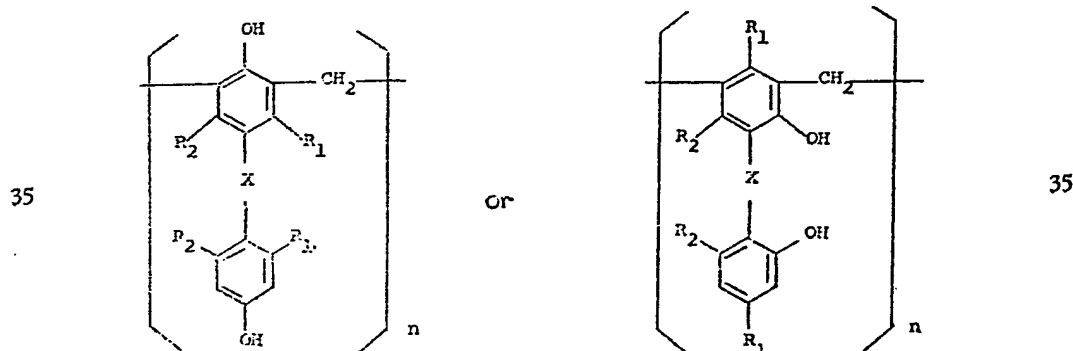
The light-sensitive composition according to the present invention is favorable in storability, excellent in film-forming ability and free from the dissolution loss of image portion during development. Furthermore, a relief image obtained by the use of the composition of the present invention is also excellent in acid resistance, oleophilic property and mechanical strength which are required in the case where the image is photoengraved.

In accordance with the present invention, there is provided a light-sensitive composition characterized by containing a condensation product obtainable by reaction of (i) a sulfonyl chloride of o-benzoquinonediazide or o-naphthoquinonediazide with (ii) a bisphenol-formaldehyde resin.

In the present invention, the bisphenol-formaldehyde resin, which is used for condensation with o-benzoquinonediazide or o-naphthoquinonediazide sulfonyl chloride, is an alkali-soluble modified phenol resin of the general formula shown below which is prepared by condensing with formaldehyde one benzene nucleus of the so-called bisphenol. In the bisphenol at least one hydroxyl group exists in each of the two benzene nuclei and the two benzene nuclei have been bonded through a bridging group X. It has the formula:



wherein X is a divalent group, i.e. $-\text{CH}_2-$ (substituted or unsubstituted), $-\text{O}-$, $-\text{S}-$, $-\text{SO}-$ or $-\text{SO}_2-$, and n is an integer of 2 or more. If X represents a methylene group it may have one or two optional substituents selected from alkyl, aryl, carboxyalkyl, the carboxy portion of which may be esterified or amidated, carboxylate and carboxamido groups. Two hydrogen atoms of the methylene group may be substituted by a cyclic alkylene group. Further optionally each of the benzene rings indicated in the above structural formula can individually bear one or more substituents (additional to those shown), which may be the same or different, for example an alkyl or alkoxy group having 1 to 4 carbon atoms, a carboalkoxy, having 1 to 4 carbon atoms in the alkoxy portion thereof, a carboxy group or hydroxy group. However, bisphenols suitable for the purpose of the present invention are required to be such that at least a part of the o- and p-positions to any hydroxy group has not been substituted. The preferred bisphenol compounds having benzene ring substituents are those having the formula:



wherein each of R₁ or R₂ which may be the same or different represents a substituent as defined above. X may have any of the meanings given above.

The following are examples of the bisphenols from which the condensation products of the invention may be derived:

5	4,4'-Dihydroxydiphenylmethane	5
	4,4'-Isopropylidenediphenol	
	p,p'-sec-Butylidenediphenol	
	2,2',4,4'-Tetrahydroxydiphenylmethane	
	2,2',4,4'-Tetrahydroxydiphenylethane (1,1)	
10	2,2',4,4'-Tetrahydroxy-6,6'-dimethyldiphenylmethane	10
	2,2',4,4'-Tetrahydroxy-6,6'-dimethyldiphenylethane (1,1)	
	2,2',4,4'-Tetrahydroxy-6,6'-dimethyltriphenylmethane	
	2,2',4,4'-Tetrahydroxy-6,6'-dicarboethoxydiphenylmethane	
	2,2',4,4'-Tetrahydroxydiphenylethane (1,1)	
15	2,2',4,4'-Tetrahydroxydiphenylpropane (1,1)	15
	2,2',4,4'-Tetrahydroxydiphenylpropane (2,2)	
	2,2',4,4'-Tetrahydroxydiphenyl-n-butane (1,1)	
	2,2',4,4'-Tetrahydroxydiphenyl-n-pentane (1,1)	
	2,2',4,4'-Tetrahydroxydiphenyl-cyclohexane (1,1)	
20	2,2',4,4'-Tetrahydroxytriphenylmethane	20
	2,2',4,4',4''-Pentahydroxytriphenylmethane	
	2,2'-Dihydroxy-4,4'-dimethoxydiphenylmethane	
	2,2'-Dihydroxy-4,4'-dimethoxydiphenylethane (1,1)	
	2,2'-Dihydroxy-4,4'-dimethyldiphenylmethane	
25	2,2'-Dihydroxy-4,4'-dimethyldiphenylethane (1,1)	25
	2,2'-Dihydroxy-4,4'-dimethoxytriphenylmethane	
	4,4'-Bis(p-hydroxyphenyl) butyric acid	
	2,2',4,4'-Tetrahydroxydiphenylsulfide	
	2,2',4,4'-Tetrahydroxydiphenylsulfoxide	
30	2,2',4,4'-Tetrahydroxydiphenylsulfone	30
	2,2',4,4'-Tetrahydroxydiphenyloxide	
	2,2',6,6'-Tetramethyl-4,4'-dihydroxydiphenylpropane(2,2)	

The alkali-soluble modified phenol resin used in the present invention is the product which is obtainable by the condensation reaction of the above-mentioned bisphenol with formaldehyde. The resin will normally have been actually obtained in this way. Preferably, 0.85 to 1.0 mole of formaldehyde is used per mole of the bisphenol, and the two are condensed with each other either as they are or in the form of aqueous solutions, using as a catalyst an acid such as hydrochloric acid or oxalic acid or an alkali such as sodium hydroxide or aqueous ammonia, while sometimes controlling the reaction by use of a solvent such as ethanol or 2-methoxyethanol.

Procedures for preparing alkali-soluble modified phenol resins by the condensation of bis-phenols with formaldehyde are set forth below in Preparation Examples.

Preparation Example 1

A mixture comprising 45.6 g. (0.2 mole) of 4,4'-isopropylidenediphenol, 16.2 g. (0.2 mole) of 37% formalin and 20 ml. of ethanol is heated at 100°C. to form a solution. To this solution is added 1.1 ml. of 1N hydrochloric acid and the reaction is continued for 25 minutes. Subsequently, the solution is gradually elevated in temperature to remove the solvent, and then dehydrated at a maximum temperature of 160°C. for 10 minutes to obtain a resin in a yield of 101.5%. This resin is slightly red, thermofusible and easily soluble in caustic alkali, alcohol and dioxane.

Preparation Example 2

A mixture comprising 54.8 g. (0.27 mole) of 2,2',4,4'-tetrahydroxy-6,6'-dimethyldiphenylethane (1,1), 14.0 g. (0.17 mole) of 37% formalin and 30 ml. of ethanol is heated at 100°C. to form a solution. This solution is mixed with 250 mg. of oxalic acid and the reaction is continued for 30 minutes. Subsequently, the solvent and formed water are removed by distillation at 120°C. to obtain a pale yellow resin in a yield of 105%. This resin is thermofusible and easily soluble in caustic alkali, alcohol and dioxane.

In the above manner, other bisphenols may also be condensed with formaldehyde to obtain desired resins.

Concrete procedures for the synthesis of condensation products of the above-mentioned resins with sulfonyl chloride of o-benzoquinonediazide or o-naphthoquinonediazide are shown below with reference to synthesis examples.

Synthesis Example 1

5 7.2 Grams of 4,4'-isopropylidenediphenol-formaldehyde resin and 8.0 g. of 1,2-naphthoquinonediazide-(2)-5-sulfonyl chloride are dissolved in 72 ml. of dioxane. To this solution is gradually added with stirring at room temperature 34 ml. of a 1N sodium carbonate solution so as to maintain the solution at below pH 8. Thereafter, the reaction is further continued for 30 minutes, and the liquid reaction mixture is poured into dilute hydrochloric acid to precipitate an oily substance. The precipitated oily substance is separated by decantation and then stirred together with a large amount of water to deposit a solid. This solid is separated by filtration, washed with methanol, dried at below 45°C., dissolved in 60 ml. of 2-methoxyethanol, filtered and then poured into a large amount of water with stirring to deposit a powdery precipitate. The deposited precipitate is separated by filtration and then dried at below 45°C. to obtain a yellowish brown powdery condensation product which decomposes at 100°C. and which does not melt even at above 300°C. yield 12.8 g. This condensation product is insoluble in alkali, easily soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Synthesis Example 2

20 9.6 Grams of 4,4'-isopropylidenediphenol-formaldehyde resin and 5.4 g. of 1,2-naphthoquinonediazide-(2)-4-sulfonyl chloride are dissolved in 80 ml. of dioxane. This solution is heated to 40° to 45°C., and 20 ml. of a 1N sodium carbonate solution is gradually added thereto with stirring so as to maintain the solution at below pH 8. Thereafter, the reaction is further continued for 1 hour, and the liquid reaction mixture is poured into dilute hydrochloric acid to precipitate an oily substance. The precipitated oily substance is separated by decantation and then stirred together with a large amount of water to deposit a solid in a short period of time. This solid is separated by filtration, washed with methanol, dried at below 45°C., dissolved in 60 ml. of 2-methoxyethanol, filtered and then poured into a large amount of water with stirring to deposit a powdery precipitate in a short period of time. The powdery precipitate is separated by filtration, washed with methanol and then dried at below 45°C. to obtain a yellow powdery resin which decomposes at 100°C. and which does not melt even at above 300°C., yield 18.4 g. This resin is insoluble in alkali, easily soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Synthesis Example 3

40 10.9 Grams of 2,2',4,4'-tetrahydroxydiphenylpropane(1,1)-formaldehyde resin and 10.7 g. of 1,2-naphthoquinonediazide-(2)-5-sulfonyl chloride are dissolved in 100 ml. of dioxane. To this solution is gradually added with stirring at room temperature 40 ml. of a 1N sodium carbonate solution so as to maintain the solution at below pH 8. Thereafter, the reaction is further continued for 30 minutes, and the liquid reaction mixture is poured into dilute hydrochloric acid to precipitate an oily substance. The oily substance is separated by decantation and then washed with water while stirring the oily substance to deposit a solid in a short period of time. This solid is separated by filtration, dried at below 45°C., dissolved in 85 ml. of 2-methoxyethanol and then poured into water to form a solid precipitate. The thus formed solid precipitate is separated by filtration, washed with methanol and then dried at below 45°C. to obtain a yellowish powdery resin which decomposes at about 100°C. and which does not melt even at above 300°C., yield 18.4 g. This resin is insoluble in alkali, easily soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Synthesis Example 4

55 14.4 Grams of 2,2',4,4'-tetrahydroxy-6,6'-dimethyldiphenylethane (1,1)-formaldehyde resin and 13.4 g. of 1,2-naphthoquinonediazide-(1)-4-sulfonyl chloride are dissolved in 120 ml. of dioxane. This solution is heated to 40° to 45°C. and 50 ml. of a 1N sodium carbonate solution is gradually added thereto with stirring so as to maintain the solution at below pH 8. Thereafter, the reaction is further continued for 30 minutes, and the liquid reaction mixture is poured into dilute hydrochloric acid to precipitate an oily substance. The precipitated oily substance is separated by decantation and then stirred together with a large amount of water to deposit a

solid in a short period of time. This solid is separated by filtration, washed with methanol, dried at below 45°C., dissolved in 100 ml. of 2-methoxyethanol and then poured into water to form a solid precipitate in a short period of time. The thus formed solid precipitate is separated by filtration and then dried at below 45°C. to obtain a yellow powdery resin which decomposes at about 100°C. and which does not melt even at above 300°C., yield 23.4 g. This resin is insoluble in alkali, easily soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Synthesis Example 5

11.4 Grams of 4,4-bis(p-hydroxyphenyl) butyric acid-formaldehyde resin and 8.0 g. of 1,2-naphthoquinonediazide-(2)-5-sulfonyl chloride are dissolved in 130 ml. of dioxane. To this solution is added with stirring at room temperature 70 ml. of a 1N sodium carbonate solution so as to maintain the solution at a weakly alkaline pH. After further stirring for 30 minutes, the liquid reaction mixture is poured into 500 ml. of water containing 5 ml. of concentrated hydrochloric acid, whereby the resin precipitates. The liquid reaction mixture is allowed to stand for a while to deposit a solid, which is then separated by filtration, washed with methanol, dried at below 45°C., dissolved in 110 ml. of 2-methoxyethanol, filtered and then poured into a large amount of water to deposit a solid precipitate in a short period of time. This precipitate is separated by filtration, washed with methanol and then dried at below 45°C. to obtain a pale yellow powdery resin which decomposes at 100°C. and which does not melt even at above 300°C., yield 15.6 g. This resin is insoluble in alkali, soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Synthesis Example 6

10.1 Grams of 2,2',4,4'-tetrahydroxydiphenylsulfide-formaldehyde resin and 10.7 g. of 1,2-naphthoquinonediazide-(2)-5-sulfonyl chloride are dissolved in 150 ml. of dioxane. To this solution is gradually added with stirring at 40° to 45°C. 40 ml. of a 1N sodium carbonate solution so as to maintain the solution at below pH 8. After further stirring for 30 minutes, the liquid reaction mixture is poured into dilute hydrochloric acid to precipitate an oily substance. The precipitated oily substance is separated by decantation and then stirred together with a large amount of water to precipitate a solid in a short period of time. This solid is separated by filtration, washed with methanol, dried at below 45°C., dissolved in 100 ml. of 2-methoxyethanol, filtered and then poured into a large amount of water to deposit a solid precipitate. Subsequently, the solid precipitate is separated by filtration, washed with methanol and then dried at below 45°C. to obtain a yellowish brown powdery resin which gradually decomposes at 100°C. and which does not melt even at above 300°C., yield 21.8 g. This resin is insoluble in alkali, easily soluble in 2-methoxyethanol and difficultly soluble in methanol and ethanol.

Condensation products of other exemplified resins can also be synthesized according to the same procedures as in the above-mentioned synthesis examples. These condensation products can be used singly, but may sometimes be mixed in optional proportions with alkali-soluble novolak resins. When the mixing ratio of said two kinds of resins is varied, the alkali solubility of the resulting light-sensitive layer with an aqueous alkaline solution may be freely controlled whereby any desired developability is obtained.

The above-mentioned condensation product is dissolved in an organic solvent such as acetone, dioxane, 2-methoxyethanol, 2-ethoxyethanol, methyl ethyl ketone, 2-butoxyethanol or 2-methoxyethyl acetate, and the resulting light-sensitive liquid composition is coated according to such coating procedure as rotary drum coating, spraying, dipping, roll coating or flow coating on a suitable support such as aluminum plate, zinc plate, copper plate, magnesium plate, plastics film or paper and is then dried to prepare a PS plate. In this case, it is preferable that the proportion of the condensation product is 0.1 to 20 parts by weight and that of the alkali-soluble novolak resin is 0 to 10 parts by weight per 100 parts by weight of the organic solvent. The above-mentioned light-sensitive composition may be incorporated with various additives which have been used hitherto.

The light-sensitive composition of the present invention has such characteristics that at the unexposed portions, resistance to an aqueous alkaline solution can be provided due to the alkali-resistance of the condensation product, while at the exposed portions, the o-quinonediazide is converted into the corresponding carboxylic acid by action of light and the said acid is easily eluted in an aqueous alkaline solution to form an image.

The light-sensitive composition is quite stable, and is storable for more than a

year when stored in a dark place. Further, a PS plate, which is obtained by coating the present composition on a support followed by drying, is also storable for more than a year when stored in a cold and dark place. In actual use of the said PS plate, there may be adopted various processes. For example, an original bearing a line or dot image is closely contacted with the light-sensitive surface of the PS plate, and the resulting assembly is exposed to light. Then, the plate is developed with an aqueous alkaline solution, whereby a positive-positive type relief image can be obtained. As a light source preferable for exposure, there is used any of carbon arc lamp, xenon lamp, mercury lamp, chemical lamp, photographic flash lamp and tungsten lamp. Typical examples of the aqueous alkaline solution used for the development are aqueous solutions of sodium hydroxide, potassium hydroxide, calcium hydroxide, sodium carbonate, potassium carbonate, sodium metaborate, sodium bicarbonate, potassium bicarbonate, sodium phosphate, sodium hydrogen phosphate, sodium phosphate, sodium hydrogen phosphate, sodium metasilicate and sodium formate. In this case, the concentration of the compound varies depending on the kind thereof, but is preferably in the range from 0.1 to 10% by weight. The thus obtained relief image is high in acid resistance and is strong against an etching solution of nitric acid or ferric chloride, so that it is successfully usable for letterpress printing plate, intaglio printing plate, name plate or print wiring. Further, the relief image is not only favorable in affinity for oils so as to be usable for lithographic printing plate, but also is high in printing resistance. Thus, a PS plate prepared by use of the light-sensitive composition is quite useful.

The present invention is illustrated in further detail below with reference to Examples, but the scope of the invention is not limited to these Examples.

Example 1

80 Grams of the condensation product of 7.2 parts by weight of 4,4'-isopropylidenediphenolformaldehyde resin with 80 parts by weight of 1,2-naphthoquinonediazide-(2)-5-sulfonyl chloride (Synthesis Example 1) and 2 g. of Methyl Violet were dissolved in one liter of 2-methoxyethanol, and the resulting solution was filtered to form a light-sensitive liquid. This light-sensitive liquid was coated by use of a rotary coating means on a zinc plate and then dried to prepare a PS plate. The sensitive surface of the thus prepared PS plate was closely contacted with a positive original, and the assembly was set in a vacuum printing frame and exposed to a fluorescent lamp for 5 minutes. Subsequently, the exposed plate was developed with a 1% aqueous sodium hydroxide solution, whereby the exposed portions were dissolved and removed to give a positive resist image excellent in mechanical strength and acid resistance. This image was washed with water, dried in a hot dry air stream and then heated at 160°C. for 2 minutes. The thus treated zinc plate was subjected to powderless etching by means of a nitric acid high speed etching machine using a surface active agent to obtain a practically acceptable photographic relief plate for printing.

Example 2

70 Grams of the condensation product of 14.4 parts by weight of 2,2',4,4'-tetrahydroxy-6,6'-dimethyldiphenylethane (1,1)-formaldehyde resin with 13.4 parts by weight of 1,2-naphthoquinonediazide-(1)-4-sulfonyl chloride (Synthesis Example 4) and 70 g. of alkali-soluble m-cresol-formaldehyde novolak resin were dissolved in one liter of 2-methoxyethanol, and the resulting solution was filtered to form a light-sensitive liquid. This light-sensitive liquid was coated, while being dried at about 60°C., by use of a rotary coating means on a copper plate having a thoroughly polished surface so as to form a uniform film. The thus obtained light-sensitive plate was stored in a cold and dark place, whereby the plate was storable for more than a year. The sensitive surface of this light-sensitive plate was closely contacted with a positive original, and the plate was exposed to a chemical lamp for 5 minutes. Subsequently, the exposed plate was developed with an aqueous alkaline solution prepared by dissolving 50 g. of sodium phosphate and 5 g. of sodium hydroxide in one liter of water, while shaking the plate in a vat containing the said solution, whereby the exposed portions were dissolved and removed to give a positive resist image. After thorough water-washing and drying, the plate was subjected as it was to the so-called Dow type etching using a ferric chloride solution, whereby an excellent relief printing plate was obtained.

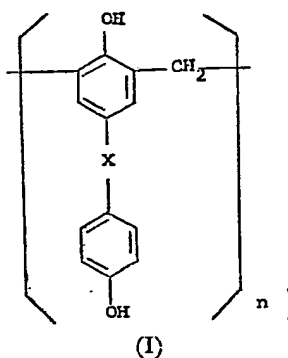
Example 3

100 Grams of the condensation product of 9.6 parts by weight of 4,4'-isopropylidenediphenolformaldehyde resin with 5.4 parts by weight of 1,2-naphthoquinonediazide-(2)-4-sulfonyl chloride (Synthesis Example 2) was dissolved in one liter of 2-

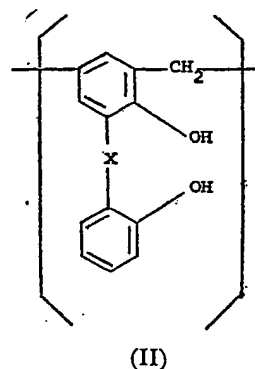
methoxyethanol, and the resulting solution was filtered to form a light-sensitive liquid. This light-sensitive liquid was coated on a grained aluminum plate to prepare a light-sensitive plate. The sensitive surface of the thus prepared light-sensitive plate was closely contacted with a positive original, and the assembly was set in a vacuum printing frame and exposed for 2 minutes to a 30 ampere carbon arc lamp at a distance of 50 cm. Subsequently, the exposed plate was dipped in and developed with a 6% aqueous sodium metasilicate solution, whereby the exposed portions were dissolved and removed to give an excellent image. After thorough water-washing, the plate was rendered hydrophilic and then subjected to an offset printer using water for moistening, thereby to obtain a large number of excellent copies of said image.

WHAT WE CLAIM IS:—

1. A condensation product obtainable by reaction of (i) a sulphonyl chloride of o-benzoquinonediazide or o-naphthoquinonediazide with (ii) a bisphenol-formaldehyde resin of the following principal structure:

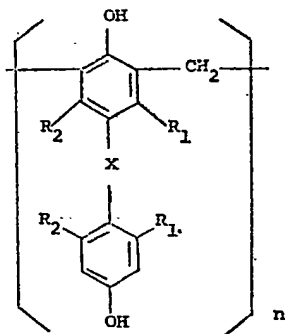


or

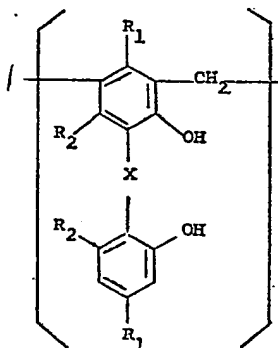


wherein the benzene rings are unsubstituted other than as shown or bear other substituents than as shown. X represents a substituted or unsubstituted methylene group or —O—, —S—, —SO— or —SO₂—, and n is an integer of 2 or more.

2. A condensation product according to Claim 1, wherein the bisphenol-formaldehyde resin has the general formula:



or



wherein X represents —CH₂—, —O—, —S—, —SO— or —SO₂—, or a methylene group in which one or two hydrogen atoms are substituted by an alkyl group, an aryl group, a carboxyalkyl group whose carboxyl portion may be esterified or amidated or two hydrogen atoms are substituted by a cyclic alkylene group; each of R₁ and R₂, which may be the same or different, represents a hydrogen atom, an alkyl or alkoxy group having 1 to 4 carbon atoms, a carboalkoxy group having 1 to 4 carbon atoms in the alkoxy portion thereof, a carboxy group or a hydroxy group; and n is an integer of 2 or more.

3. A condensation product according to Claim 1 or 2 wherein reactant (i) is 1,2-naphthoquinone diazide-(2)-4-sulphonyl chloride or 1,2-naphthoquinone diazide-(2)-5-sulphonyl chloride.

4. A condensation product obtainable by reaction of (i) any one of the sulphonyl chlorides of the quinonediazides hereinbefore mentioned with (ii) any one of the phenol-formaldehyde resins hereinbefore listed conforming to formula (I) or (II) given in claim 1.
- 5 The condensation products obtained from any one of the synthesis Examples hereinbefore set forth. 5
6. A light-sensitive composition containing a condensation product claimed in any preceding claim.
7. A light-sensitive composition according to Claim 6, further containing an alkali-soluble novolak resin. 10
8. A light-sensitive composition according to Claim 6 or 7, further containing acetone, dioxane, 2-methoxyethanol or 2-ethoxyethanol.
9. A light-sensitive composition according to Claim 8 containing 0.1—20 parts by weight of the condensation product and 0 to 10 parts by weight of the novolak resin per 100 parts by weight of the organic solvent. 15
10. A support carrying a layer of a composition claimed in any one of claims 6—9.
11. A method of preparing a photographic relief printing plate which comprises coating a light-sensitive composition claimed in any one of claims 6—9 on a support, subjecting the resulting presensitized plate to imagewise exposure to light, and treating the exposed plate with an aqueous alkaline solution. 20
12. A printing plate obtained by a method claimed in claim 11.
13. A method of preparing a photographic relief printing plate which comprises coating on a support a light-sensitive composition containing a condensation product claimed in claim 2, subjecting the resulting presensitized plate to imagewise exposure to light, and treating the exposed plate with an aqueous alkaline solution. 25
14. A printing plate obtained by a method claimed in claim 13.
15. A photo-resist process employing a photo-resist material comprising a condensation product claimed in claim 1.
16. A photo-resist process employing a photo-resist material comprising a condensation product claimed in claim 2. 30

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square,
Gray's Inn,
London WC1R 5EU.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.